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Effect of Finite Thickness on Elasticity Determination using Atomic Force Microscope

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Effect of Finite Sample Thickness on Elasticity Determination Using Atomic Force Microscopy

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Abstract

The effect of finite sample thickness on material elasticity measurements made using an Atomic Force Microscope (AFM) has been calculated. The model includes an elastic layer on an elastic foundation and simulates sample indentation under an applied load, for rigid axisymmetric tips with conical, paraboloidal, and hyperboloidal profiles. The results show that a common approach to estimating elastic modulus from force-displacement curves can lead to significant error that depends on the units of measurement. A method to estimate this error unambiguously and correct it is proposed. In addition, it is shown that elasticity estimates for monolayer thick samples using the force-modulation technique have substantial, sample thickness-dependent error. Local thickness variation can result in misleading contrast in force modulation images for samples that are several nanometers thick.

Atomic Force Microscopy (AFM) measurements are often made on thin film samples with thickness ranging from few nanometers to microns. Quantitative elasticity measurements using AFM are usually interpreted assuming semi-infinite sample geometry. [1-12] In this paper we model the effect of substrate on elasticity measurements made on thin films. This effect is particularly important when Young modulus mapping is performed on samples exhibiting inhomogeneous thickness variation[13], and when a breakdown of macroscopic models of elasticity is tested. The modulus of elasticity for typical polymeric and biological samples is usually several orders of magnitude smaller than the modulus of the underlying hard substrate[1]. We calculate the sample's indentation by considering a rigid axisymmetric tip under an applied load, and we report a significant error arising from the common assumption of infinite sample thickness. We consider conical, paraboloidal, and hyperboloidal tip geometries.

Presently the most common techniques for measuring elasticity with high spatial resolution are indentation measurements [1, 2, 6-12] and force-modulation [3-5] experiments, which are performed using AFM. These measurements are interpreted using a model for a paraboloidal or conical tip elastically indenting a half-space sample. However, sharp AFM tips often have a conical shape with a rounded apex (manufacturers usually specify 10 - 100 nm radius of curvature). Thus, to simulate this shape we choose a hyperboloidal tip profile. Figure **1a** shows the shapes of tips we use, Figure **1b** shows the geometry of indentation and introduces the variables and parameters we use later in this article.

The elastic modulus for a semi-infinite sample can be estimated using the load-indentation dependencies as described by Sneddon. [14]

$$F = \frac{2E\tan(\alpha)}{\pi(1-\sigma^2)}\delta^2 \tag{1a}$$

$$F = \frac{4E\sqrt{R}}{3(1-\sigma^2)}\delta^{\frac{3}{2}} \tag{1b}$$

$$\left.\begin{aligned} \delta &= \frac{a^2}{2R}\xi\left[\frac{\pi}{2} + \arctan\left(\frac{1}{2\xi} - \frac{\xi}{2}\right)\right] \\ F &= \frac{Ea^3}{(1-\sigma^2)R}\left[\xi^2 + \frac{\xi}{2}\left\{\frac{\pi}{2} + \arctan\left(\frac{1}{2\xi} - \frac{\xi}{2}\right)\right\}(1-\xi^2)\right] \\ \textit{where} \quad \xi &= \frac{R\cot(\alpha)}{a} \end{aligned}\right\} \tag{1c}$$

Equations **1a-c** correspond to conical, paraboloidal and hyperboloidal shapes of revolution, respectively. Here F is load, δ – indentation, a- contact area radius, R – tip radius of curvature, α – tip semi-vertical angle, E - Young modulus, σ – Poisson ratio, as illustrated in Figure 1. From Equations **1a-b** it may be seen that a linear fit in log(F) vs. log(δ) coordinates has an intercept related to the Young modulus:

$$\log(F) = \log\left(\frac{2E\tan(\alpha)}{\pi(1-\sigma^2)}\right) + 2\log(\delta) \tag{2a}$$

$$\log(F) = \log\left(\frac{4E\sqrt{R}}{3(1-\sigma^2)}\right) + \frac{3}{2}\log(\delta) \tag{2b}$$

We first note that using Equation **2a** (conical shape) for tips with rounded apexes results in considerable error. For example, in order to estimate the Young modulus within a factor of two (using hyperboloidal tip with 20° semi-vertical angle and 10 nm radius of curvature, according to Equations **1c**) the maximum indentation should be *larger* than 2.5 μm. On the other hand, Equation **2b** gives factor of two error for indentations that are *ca* 400 nm using the same parameters. This is anticipated since Equations **1c** transform into **1a** when $R \ll a \cdot \tan(\alpha)$, and into **1b** when $a \ll R\cot(\alpha)$.

It is intuitively clear that if a soft sample rests on a hard foundation, then the tip starts to "feel" substructure when the radius of contact area is comparable to the sample's thickness. [15] This results in force-indentation curves that are non-linear in logarithmic coordinates. Figure 2 is an explicit illustration of such an effect. The Figure shows the indentation of a ~30 nm thick spin-cast sample of coblock (polystyrene-polyvinylpyridine) polymer on a microscope coverslip substrate.[16] The tip radius was approximately 60 nm.

For this type of response, Young modulus estimates can have an error that varies with the units of measurements. Indeed, the error depends upon the distance between intercept of the linear fit line (δ=*1 unit*) and the line corresponding to the conditions assumed when deriving Equations **1**. As illustrated in Figure 2, such an error can even change sign. Using the units shown on Figure 2, the estimated modulus would be two times smaller than the modulus obtained when *a/h* value is small.

To clarify this problem we have performed numerical calculations, which simulate the indentation of an elastic layer bonded to an elastic foundation. Our computations are based on an elastic layer model by Dhaliwal and Rau [17]. Force-indentation curves are obtained by solving a Fredholm integral Equation of the second kind:

$$\phi(t)+\frac{a}{h\pi}\int_0^1 K(x,t)\phi(x)dx=-\frac{Ea}{2(1-\sigma^2)}\frac{d}{dt}\left[\int_0^t\frac{\delta-f(x)}{\sqrt{t^2-x^2}}x \quad dx\right],\quad 0\le t<1 \qquad \textbf{(3)}$$

where $K(x,t)$ is the kernel of the integral Equation, E and σ are the Young modulus and the Poisson ratio of the layer, respectively. The kernel is defined as:

$$K(x,t)=2\int_0^\infty H(2u)\cos\left(\frac{a}{h}tu\right)\cos\left(\frac{a}{h}xu\right)du$$

with

$$H(x) = -\frac{b + c(1+x)^2 + 2bce^{-x}}{e^x + b + c(1+x^2) + cbe^{-x}},$$
$$b = \frac{(3-4\sigma) - \mu(3-4\sigma_1)}{1+\mu(3-4\sigma_1)},$$
$$c = \frac{1-\mu}{\mu + 3 - 4\sigma}$$

μ is the ratio of Lamé constants $\mu = (E/2(1+\sigma))/(E_1/2(1+\sigma_1))$ [19], *f(x)* in Equation **(3)** is the tip shape function, and here we use the following shapes [17] :

$$\begin{aligned} f(x) &= ax\cot\alpha, && \textit{conical tip} \\ f(x) &= \frac{a^2}{2R}x^2, && \textit{paraboloidal tip} \\ f(x) &= R\cot^2\alpha\left[\sqrt{(ax/R\cot\alpha)^2+1}-1\right], && \textit{hyperboloidal tip} \end{aligned} \qquad \textbf{(4)}$$

where a is the radius of the tip-sample contact area, R - radius of the curvature of the tip apex, α - tip semi-vertical angle as shown on Figure 1.

To find the indentation δ, we use the condition that the normal component of stress remains finite around the circle of contact between the tip and the sample. A solution of **(3)** must satisfy [17]

$$\phi(1) = 0 \qquad \textbf{(5)}$$

We solve Equation **(3)** numerically to determine the indentation. For each value of the contact radius a we iteratively find the indentation δ such that the solution of **(3)** satisfies **(5)**, and we find the load force according to [17] :

$$F = -4\int_0^1 \phi(t)dt \qquad \textbf{(6)}$$

To estimate the error in the Young modulus unambiguously we plot logarithmic force indentation curves in normalized coordinate units: [18]

$$\left.\begin{aligned}\tilde{\delta} &= \frac{\delta}{h\cot(\alpha)}\\ \tilde{F} &= \frac{F(1-\sigma^2)}{2h^2\cot(\alpha)}\end{aligned}\right\}\quad \textit{conical tip} \tag{7a}$$

$$\left.\begin{aligned}\tilde{\delta} &= \frac{\delta\cdot 2R}{h^2}\\ \tilde{F} &= \frac{F\cdot R(1-\sigma^2)}{h^3}\end{aligned}\right\}\quad \textit{paraboloidal tip} \tag{7b}$$

For conical and paraboloidal tips, force *vs.* indentation curves plotted in these coordinates change only when ratio of Lamé coefficients, μ, changes. μ shows the mismatch between the rigidity modulus of the top layer and the rigidity modulus of the substrate. When $\mu=1$ and $\sigma=\sigma_1$, the kernel vanishes and Equation **3** becomes equivalent to the Abel integral equation considered by Sneddon [14]. The elastic layer indentation curves are not linear in logarithmic coordinates. Therefore, the slope and the intercept of straight lines fitted through the data points depend upon the maximum indentation value. The Young modulus can be estimated in normalized coordinates using Equations **1a** and **1b** with force and indentation substituted from Equations **7a** and **7b** for any maximum indentation value. Hereafter we use the term Young modulus to indicate the true Young modulus of the top layer material, and "estimated Young modulus" to mean the Young modulus estimated from the linear fit. We calculate the ratio of this estimated Young modulus to the modulus of the top layer (we call this ratio a reduced Young modulus) and plot it *versus* normalized maximum indentation. Plots for different values of μ are shown in Figure 3. The left panel shows a calculation for a conical tip, and the right panel shows the calculation for a paraboloidal tip. μ values are shown to the right of each curve. We used equally spaced δ values in our calculation. In the AFM experiment this is correct when the cantilever spring constant is considerably larger than the surface spring constant.

The reduced modulus from Figure 3 can be used as a correction factor to obtain a better estimate of the Young modulus for soft samples. Indeed, the lines for μ less than 10^{-3} are almost indistinguishable. Therefore these lines can be used as correction factors for samples with Young modulus ~0.1 GPa and less and substrate modulus ~100 GPa.

For larger values of μ an iterative procedure can be used to correct both E and μ. As an explicit example using the data plotted on Figure 2, we calculate $\tilde{\delta}$ and $\tilde{F}$ according to **7b**. We take σ=0.33 as a reasonable suggestion. The estimated Young modulus is calculated from the intercept of linear fit in log-log coordinates according to equation $E = 3\exp(b)/\sqrt{2}$, where b is the intercept. Thus we obtain E=133 MPa. The maximum normalized indentation is $\tilde{\delta}_{max} = 0.88$. Using Figure 3 we can conclude that E is overestimated by a factor ~2.1, thus the true modulus E=63 MPa. This value of Young modulus happens to be close to the one used to calculate the dashed line on Figure 2, 58 MPa. We note that our indentation values are not equally spaced, which contributes to inaccuracy in the modulus determination. It is important to know the layer thickness accurately to determine the correction for E (since normalized indentation in **7b** is proportional to h^{-2}). On the other hand, if the Young modulus is known, the steep dependence of $\tilde{E}$ on h can be used to estimate the layer thickness.

Force – indentation curves for a hyperboloidal tip were transformed according to Equation **7b**. The results are shown on Figure 4, which shows the reduced Young modulus plotted against the maximum normalized indentation, for $\mu \cong 0$ and different $h/(R \cot \alpha)$ ratios. If the $h/(R \cot \alpha)$ ratio is small (less than 0.1) then the hyperboloidal tip indentation curves are very close to the paraboloidal tip curve (dashed line). Also small values of normalized indentation correspond to a small ratio of maximum contact area radius to layer thickness. In this case, hyperboloidal tip indentation features are similar to paraboloidal tip indentation. Otherwise, hyperboloidal punch indentation can not be described by simple models and should be treated explicitly.

In addition, we would like to comment on the use of the force modulation method to determine the elasticity of thin layers. In this method the sample oscillates at a certain frequency, and this oscillation is sensed by the tip, which contacts the sample. The amplitude of the tip oscillation depends upon a sample stiffness and, for a semi-infinite sample, the Young modulus can be estimated using the following Equation [5]:

$$E = \sqrt{\frac{\left(k_c(z/\delta - 1)\right)^3}{6RF}} \tag{8}$$

where k_c is cantilever spring constant, R – tip radius of curvature, F – average load applied to the sample, z – modulation amplitude of the sample, δ – tip oscillation amplitude. For a thin sample such an estimate can result in substantial error. Figure 5 shows the reduced Young modulus estimated according to Equation 8 *vs.* applied load for samples of different thickness. The calculation parameters are given in the figure's caption. Figure 5 demonstrates that a change in the sample thickness may result in an apparent softness contrast in force-modulation images.

Figure 6 shows the same dependence as Figure 5, where the lines are calculated in normalized coordinates using Equations **7b** and **8** for several values of μ. If the layer thickness, tip radius and elastic parameters of substrate (E_1, σ_1) are known and a reasonable assumption about Poisson ratio of elastic layer can be made, the reduced elastic modulus from Figure 6 can be used to correct the error in measured modulus. Since we do not know correct value for μ (it depends on true Young modulus), an iterative procedure can be employed to determine the correction coefficient $\widetilde{E}$. Let E^* be the symbol for the Young modulus, as estimated from equation 8. To obtain the correction factor for E^*, the corresponding average normalized load can be obtained from Equation 7b. This gives the fixed position on the abscissa of Figure 6. The ratio of E^* to the Young modulus of substrate (E_1) gives an approximate μ value. From Figure 6, an approximate correction factor $\widetilde{E}$ can be found, from which we find a better estimate for $\mu = E^*/(\widetilde{E} \cdot E_1)$. This gives an adjusted correction factor $\widetilde{E}$, which in turn improves the estimate of μ. The iterations converge in a few steps to a best value for μ, resulting in the correction factor for E^*. For an explicit example, we consider E^* =0.5 GPa, E_1= 100 GPa, and $\widetilde{F}$ =1. The iterative process using these parameters is shown with circles on Figure 6. Initially we have $\mu \approx 0.005$. From the figure we can see that for this μ, $\widetilde{E} \approx 3$. This decreases the estimate of μ to 0.0016, giving us $\widetilde{E} \approx 4.5$. The next step results in $\widetilde{E} \approx 5$, and subsequent iteration does not change $\widetilde{E}$ significantly. Thus, we can conclude that the true elastic modulus is close to 0.1 GPa.

In summary, we have used an elastic layer on an elastic foundation model to calculate the error associated with using elastic half-space model to estimate the Young modulus in AFM indentation and force modulation experiments. We find that the application of semi-infinite sample models can result in unpredictable and significant error in Young modulus estimates. Normalized coordinates should be used to obtain consistent results. Contrast in the force-modulation imaging may be related to inhomogeneity in the sample thickness. We have proposed a method for reducing the error related to finite sample thickness.

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Figure Captions

1. **(a)** AFM tip profiles considered in this paper. α - semi-vertical angle, R – radius of curvature of the tip apex. **(b)** Geometry of sample indentation: δ - indentation; F – load; a – contact area radius; k_c cantilever spring constant; h – sample layer thickness, E, E_1, σ, σ_1 – Young moduli and Poisson ratios of the sample layer and substrate, respectively.

2. Deviation of load-indentation from power law dependence. Force – indentation data was collected on a ~30 nm thick spin-cast sample of coblock (polystyrene-polyvinylpyridine) polymer on a microscope coverslip substrate. The tip radius was approximately 60 nm. Fitting to a straight line in logarithmic coordinates gives an error in the Young modulus which depend upon the origin that is chosen for $log(\delta)$, which is determined by the units of measurement. Here a solid line is the best linear fit to the force-indentation values that are shown as '+' symbols. The dashed line was calculated according Equation 1a with the Young modulus calculated from the data subset with a small a/h ratio. The brackets indicate a mismatch in the intercept, which is related to the error in the Young modulus (Equations 2). Two possible positions of $log(\delta)$ origin are shown.

3. X axis – normalized maximum indentation, Y axis – ratio of Young modulus estimated from linear fit to modulus of top layer. Left panel – conical tip, right panel – paraboloidal tip. Different lines correspond to different ratio of Lamé coefficients, lines ***a – g*** μ correspond to 1, 0.46, 0.22, 0.1, 0.046, 0.01, and 0.001, respectively.

4. Reduced Young modulus plotted *vs.* normalized maximum indentation for hyperboloidal tip (solid lines). Coordinates transformed according to the paraboloidal tip Equations 7b. Here μ=0.9·10^{-3}, and lines (from the top) correspond to $h/(R \cot \alpha)$ ratios: 1.7, 1.2, 0.84, 0.58, 0.36 and 0.18. For comparison we show a calculation for the paraboloidal tip (dashed line).

5. Ratio of the modulus estimated using Equation (8) to actual value given as function of average load for samples of different thickness. Different lines correspond to different layer thickness. The thickness (from 1 to 100 nm) is indicated on the graph. Other parameters: tip radius of curvature 10 nm, μ=0.01, E=1 GPa, σ=0, k_c 10 N/m, sample oscillation amplitude 0.02 nm.

6. Plots of the reduced modulus *vs.* the normalized force for different μ values illustrate a possible error in the Young modulus as determined using the force-modulation technique. Starting from the top μ: 0.001, 0.0022, 0.0046, 0.01, 0.022, 0.046, 0.1, 0.22 and 0.46. Circles show an iterative process to determine the correction factor for estimated Young modulus.

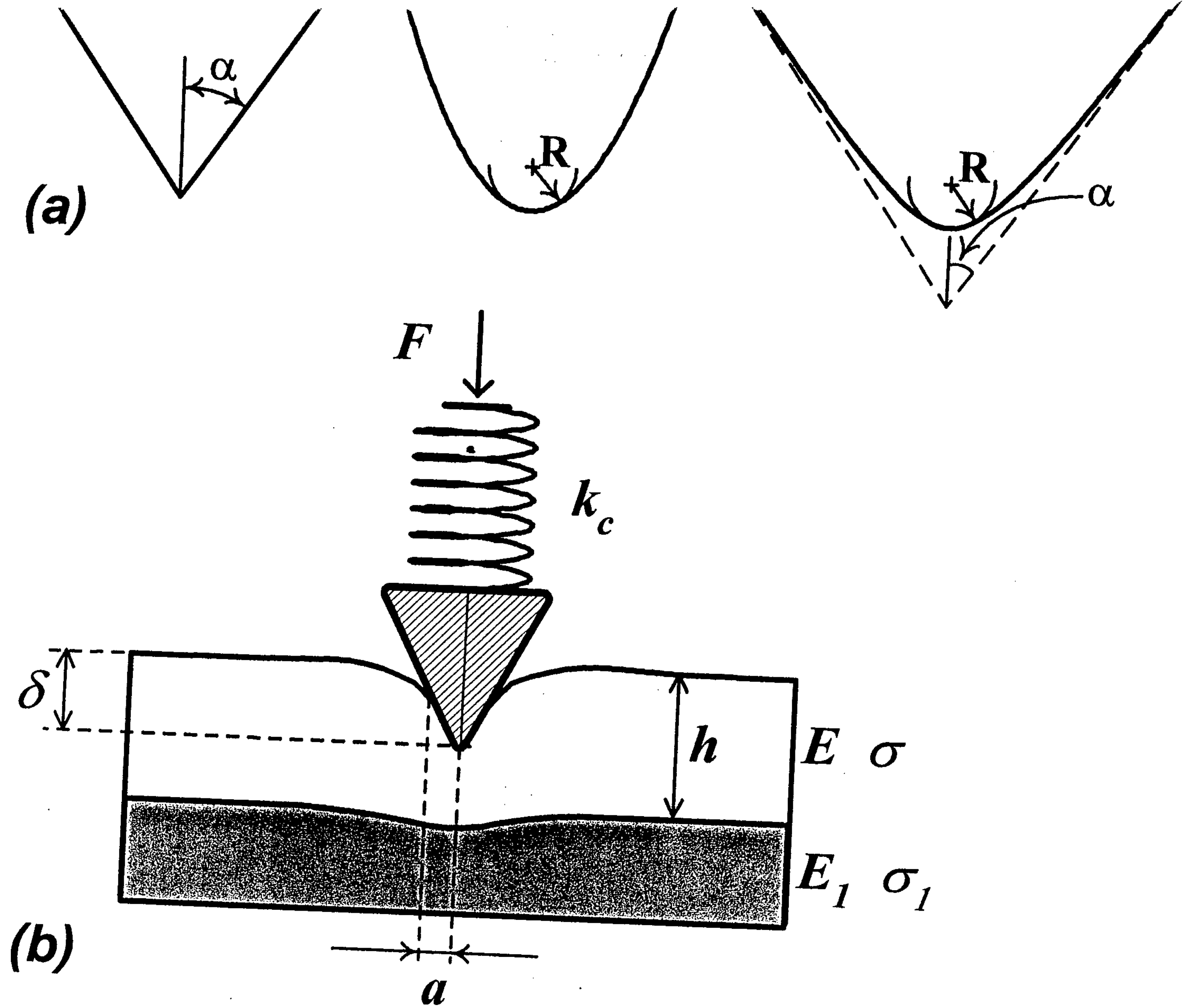


Figure 1

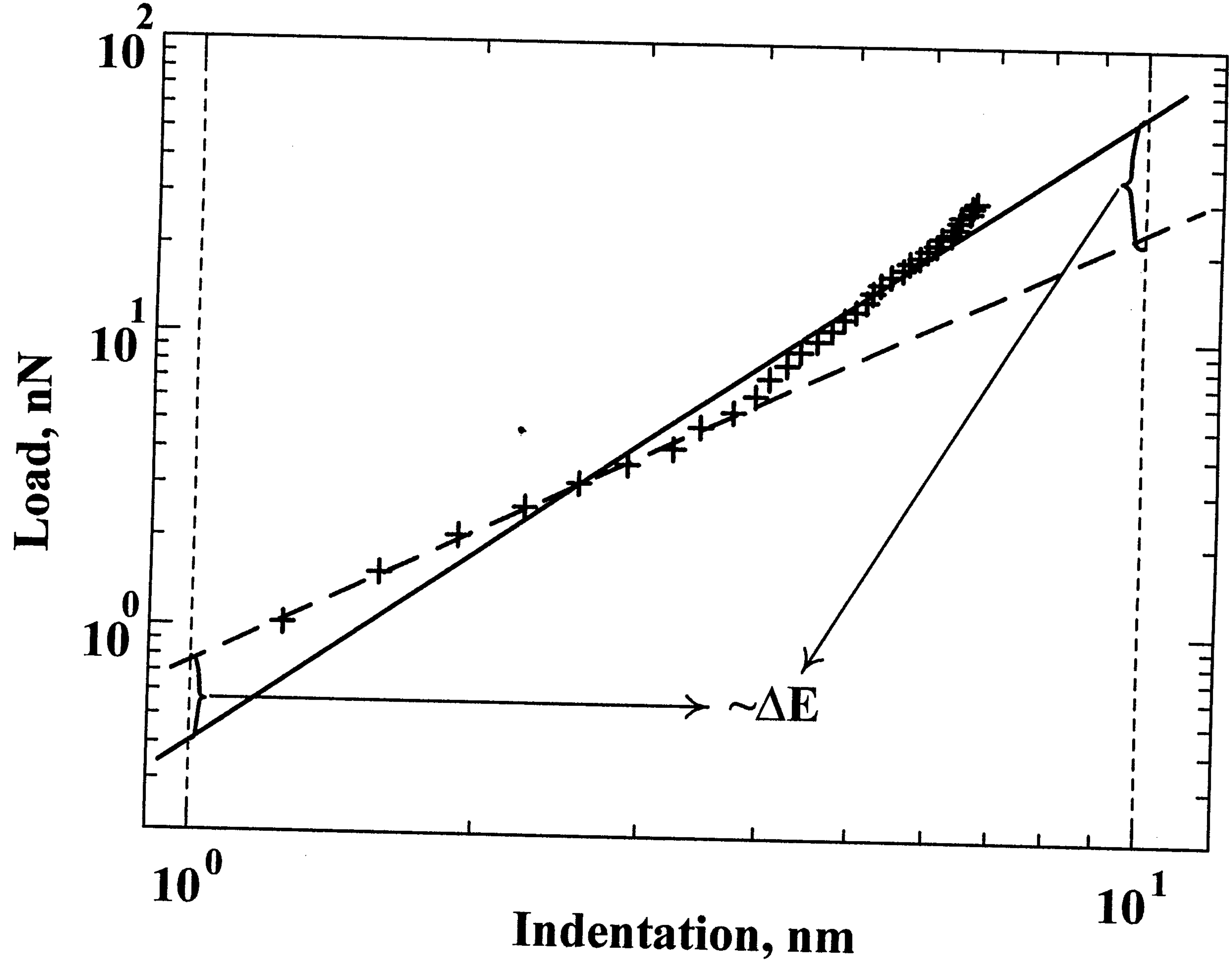


Figure 2

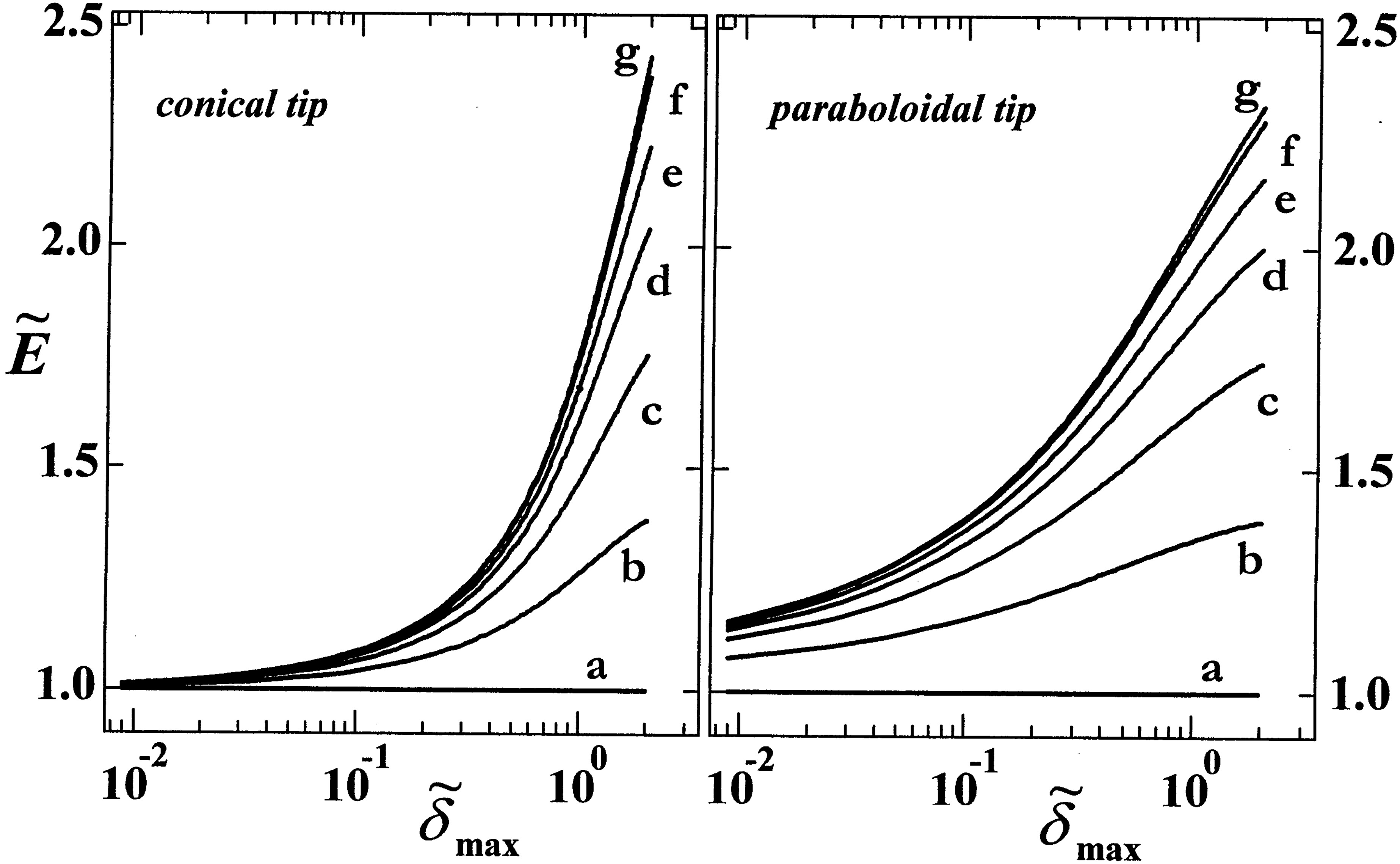

conical tip
paraboloidal tip
a
b
c
d
e
f
g
2.5
2.0
1.5
1.0
$\tilde{E}$
10^{-2}
10^{-1}
10^{0}
$\tilde{\delta}_{max}$

Figure 3

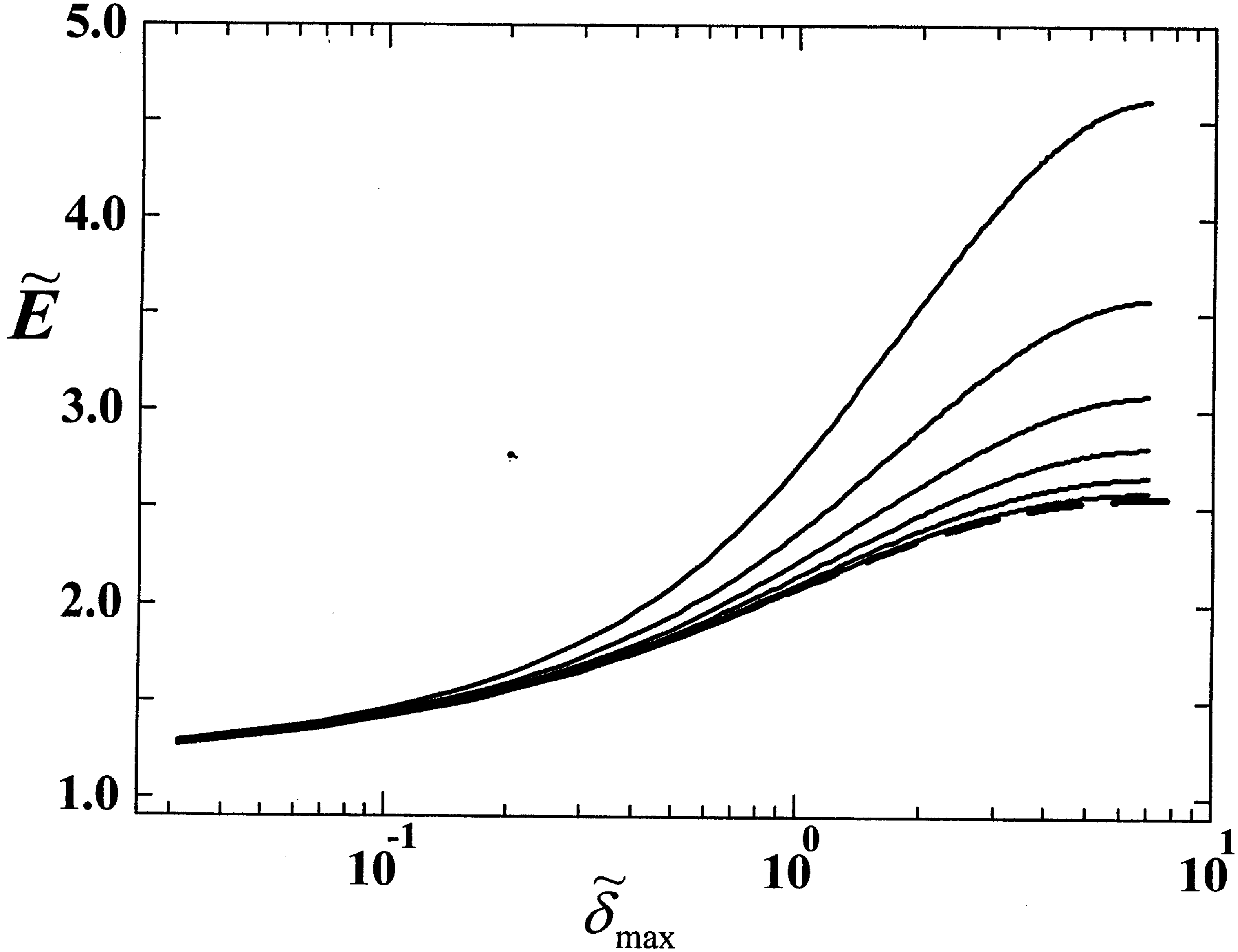
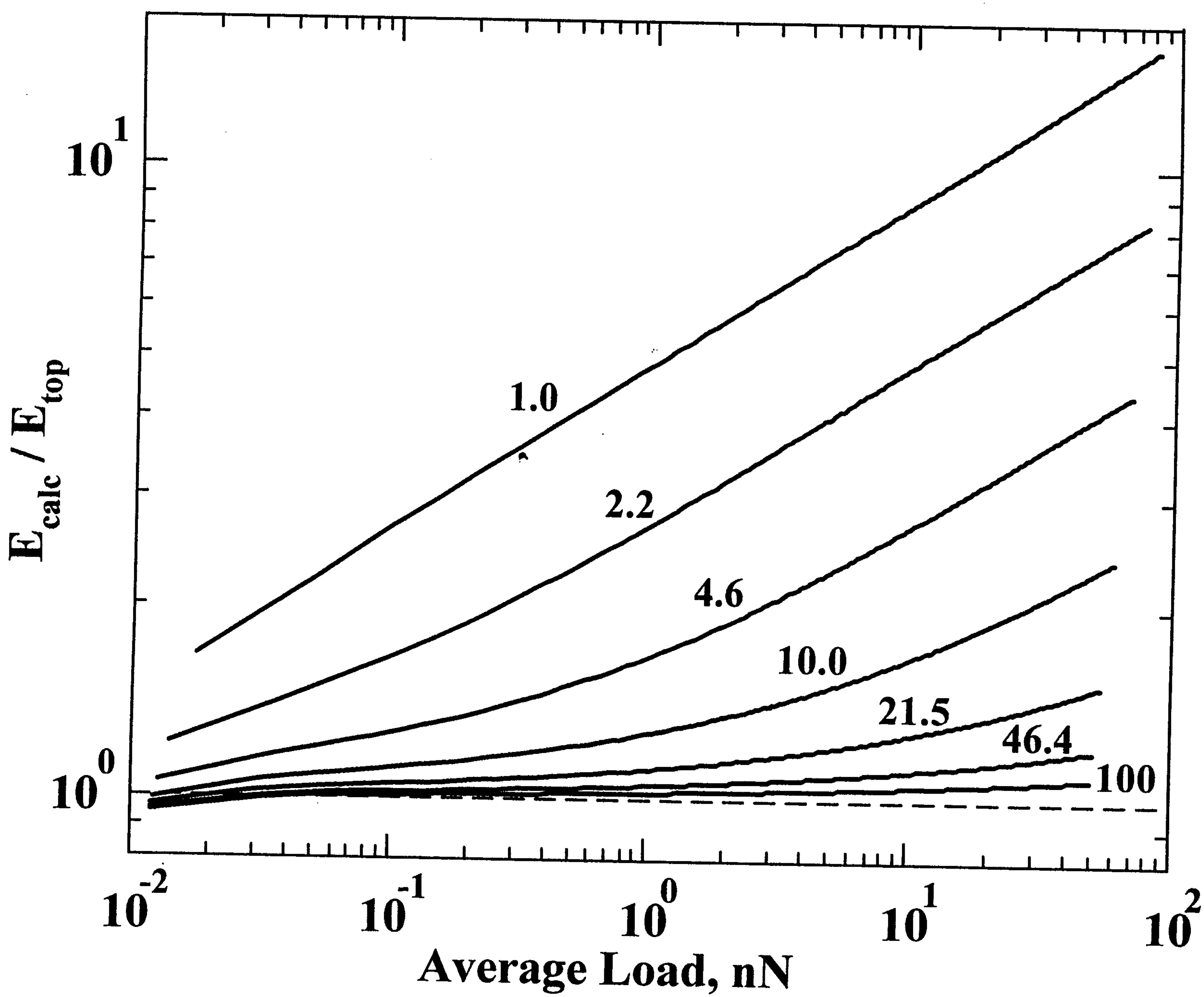


Figure 4



E_{calc} / E_{top}
10^1
10^0
1.0
2.2
4.6
10.0
21.5
46.4
100
10^{-2}
10^{-1}
10^0
10^1
10^2
Average Load, nN

Figure 5

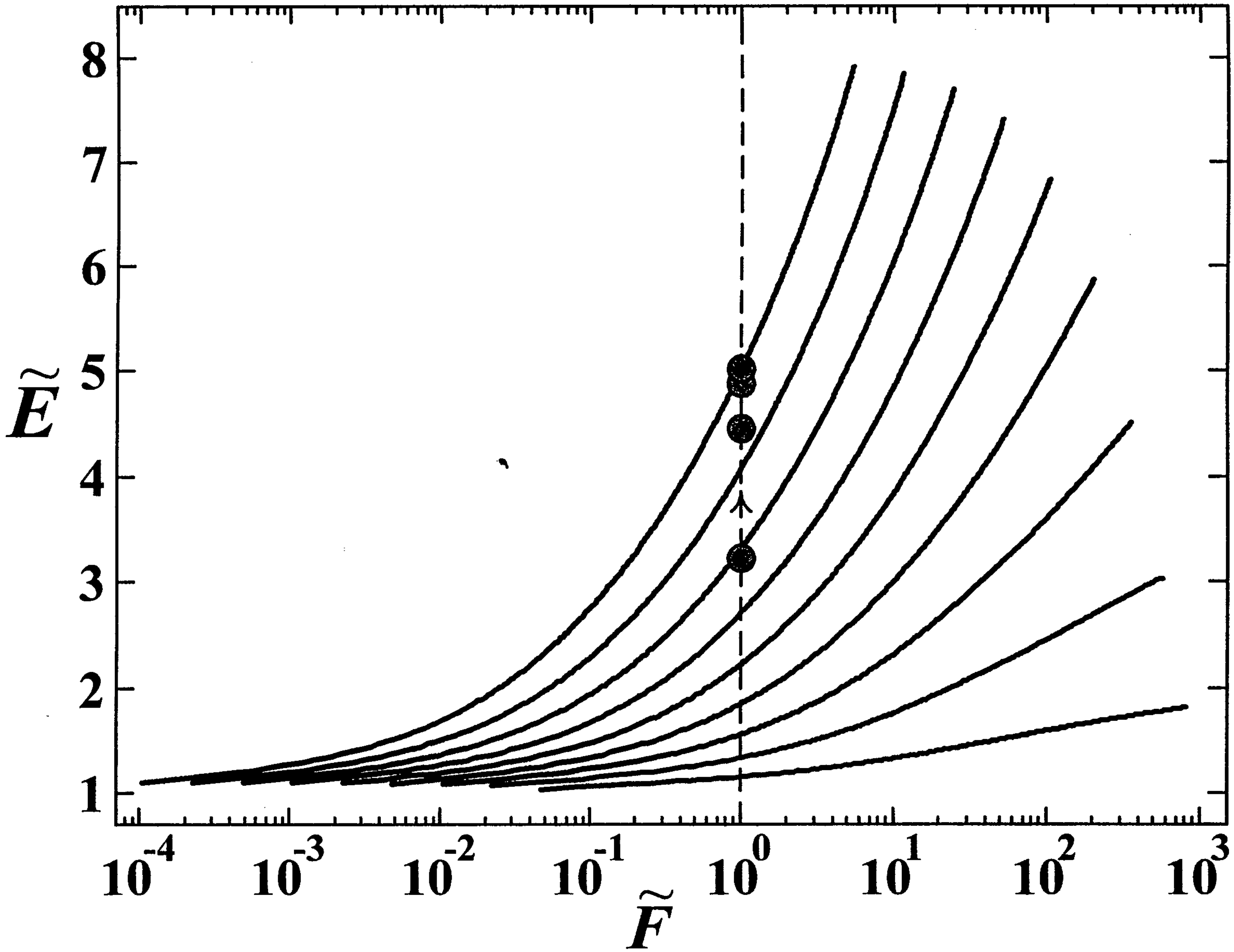


Figure 6

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